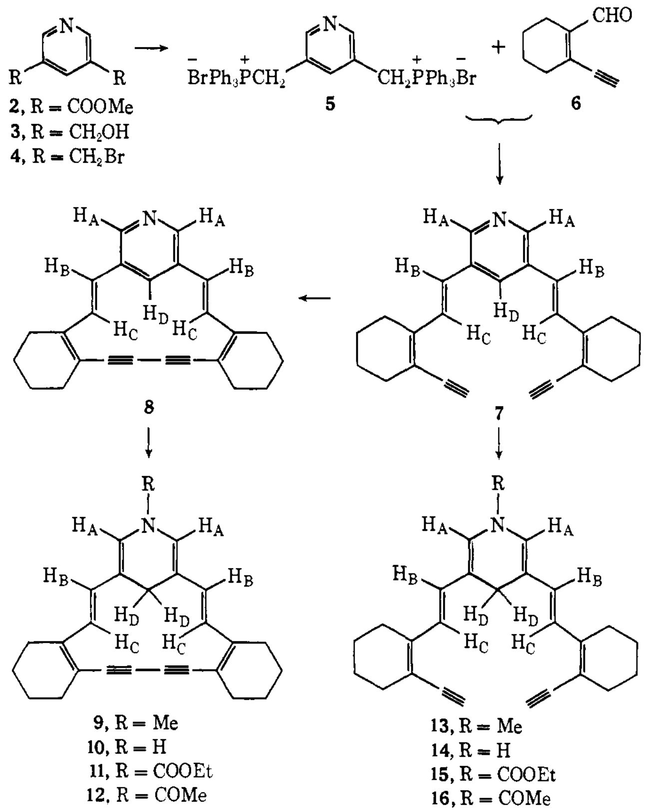

the pyridine 7, except that the N-methyl derivative **13** was obtained from **14** by reaction with NaH in dimethoxyethane and subsequent treatment with MeI.

The nmr parameters of the aza[17]annulenes **9–12**, as well as of the models **13–16**, are given in Table I. The differences in chemical shift on passing from the model to the corresponding aza[17]annulene are given in parentheses. It can be seen that substances **9–12** all exhibit a diamagnetic ring current, indicative of aromaticity, the outer protons being deshielded and the inner protons shielded.[9] As expected, the magnitude of the ring current (**9** > **10** > **11** > **12**) falls off with increasing electronegativity of the substituent. The nitrogen substituents are also affected by the diamagnetic ring current; *e.g.*, the N-methyl resonance in **9** (τ 6.35) is at lower field than that of the model **13** (τ 6.93) and is lower than even that of N-methylpyrrole (τ 6.50).

The fact that each of the substances **9–12** is considerably more stable than the corresponding models **13–16** is also in accord with their aromatic nature.[10] Moreover, the electronic spectra [main maxima ($CHCl_3$) **9**, 358; **10**, 349; **11**, 329; **12**, 331 nm; highest wavelength band, **9**, 535; **10**, 522 sh; **11**, 482 sh; **12**, 482 sh nm] may also be indicative of their aromaticity, **9** being most aromatic, and **11** and **12** being least aromatic.[11]

The observation that the aza[17]annulene derivatives **9–12** sustain a diamagnetic ring current, whereas N-ethoxycarbonylaza[17]annulene apparently does not,[3b] is presumably due to the greater planarity of the former systems, caused by the presence of the methylene bridges and/or the acetylenic linkages.

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(9) In fact, the shielding of the inner protons in **9–12** is presumably greater than indicated in Table I, since the corresponding protons in the models **13–16** are at higher field than they would be in the particular conformations indicated in the formulas (*cf.* the difference in the nmr spectra of 7 and 8, discussed above).

(10) Although the aza[17]annulene **10** was gradually reoxidized to **8** on standing in air, the corresponding reoxidation of **14** to **7** occurred much more readily.

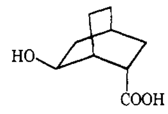
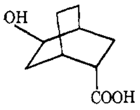
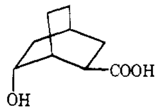
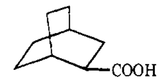
(11) Attempts to determine the pK_a values of substances **9–12** so far have given no meaningful results.

σ-Inductive Model *vs.* Field Model. Observation of a Reversed Attenuation Effect[1,2]

Sir:

Many attempts have been made to distinguish between and evaluate the relative importance of the σ-inductive and field models.[3] Perhaps the strongest qualitative evidence for the operation of field effect is the observation of the angular dependence of substituent effects.[4] Several studies involving direct comparison of rigid model systems provide more quantitative evidence for the superiority of the field model in describing the propagation of nonconjugative substituent effects.[5] We now report the first unambiguous example of a reversed attenuation effect—an observation which questions the very foundation of the σ-

Table I. pK_a Values in 50% (by Weight) Aqueous Ethanol at 25°

No.	Structure	pK_a
I		6.261 ± 0.002
II		6.416 ± 0.023
III		6.470 ± 0.004
IV		6.722 ± 0.006

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(1) (a) Mechanism of Transmission of Nonconjugative Substituent Effects. III; (b) part I: C. L. Liotta, W. F. Fisher, and G. H. Greene, *Chem. Commun.*, 1251 (1969); part II: C. L. Liotta, W. F. Fisher, and C. L. Harris, *ibid.*, 1312 (1971).

(2) Abstracted in part from the Ph.D. Thesis of W. F. F., Georgia Institute of Technology, 1970, and in part from the Masters Thesis of E. L. S., Georgia Institute of Technology, 1971.

(3) J. D. Roberts and W. T. Moreland, *J. Amer. Chem. Soc.*, **75**, 2167 (1953); S. Siegel and J. M. Kormarmy, *ibid.*, **82**, 2547 (1960); L. M. Stock and H. D. Holtz, *ibid.*, **86**, 5188 (1964); F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5677 (1967); P. E. Peterson, C. Casey, E. V. Tao, A. Agatrop, and G. Thompson, *ibid.*, **87**, 5163 (1965); K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963), and references cited therein.

(4) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3548 (1962); W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967); R. Golden and L. M. Stock, *ibid.*, **88**, 5928 (1966); K. Bowden and D. C. Parkin, *Chem. Commun.*, 75 (1968); M. J. S. Dewar, *ibid.*, 547 (1968); W. Adcock and P. R. Wells, *Aust. J. Chem.*, **18**, 1351 (1965); E. J. Grubbs and R. Fitzgerald, *Tetrahedron Lett.*, 4901 (1968); D. S. Noyce and B. E. Johnston, *J. Org. Chem.*, **34**, 1252 (1969).

(5) C. L. Liotta, W. F. Fisher, and G. H. Greene, *J. Chem. Soc. D*, 1251 (1969); C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, **90**, 336 (1968).

Table II. Calculated Log K_X/K_H by Means of TMKW[a] Cavity Model

Acid	R, Å	μ, D	θ	D_E[b]	Log $(K_X/K_H)_{calcd}$	Log $(K_X/K_H)_{exptl}$
I	4.52	1.4	30° 26′	3.80	0.56	0.461
II	5.24	1.4	14° 49′	4.10	0.43	0.306
III	5.53	1.4	67° 27′	4.26	0.15	0.252

[a] Tanford modification of the Kirkwood–Westheimer cavity model. [b] Reference 13.

inductive model. We also show that the field model adequately accounts for the experimental facts.

We have synthesized some 5- and 6-hydroxybicyclo[2.2.2]octane-2-carboxylic acids[6] and determined their pK_a values in 50% (by weight) aqueous ethanol at 25°.[10] The data are summarized in Table I. In each of these cases both the substituent and the reaction center are, to a good approximation, in the same steric environment. This implies that the steric approach of solvent molecules to these centers is approximately the same in the three cases. In addition, examination of molecular models shows that there is little chance for direct steric interaction between the substituent and the reaction center. Comparison of the relative pK_a values, therefore, allows a direct evaluation of the relative polar effects of these substituents.

The σ-inductive model[11] predicts that the effect of substituents at C-6 and C-5 on a reaction center at C-2 would be $[(1/f)^2 + (1/f)^4 + 2(1/f)^6]$ and $[2(1/f)^3 + (1/f)^5]$, respectively, where f is the attenuation factor per carbon. Using factors of 2–3,[5] the predicted relative magnitude of the σ-inductive influence of a substituent at C-6 compared to C-5 would be 1.22–1.61. Comparison of I and II (Table I) shows that the inductive order is in the correct direction; however, III is less acidic than II. The σ-inductive model predicts just the opposite. This reversed attenuation effect points to an internal inconsistency in the model and casts serious doubt on its usefulness in predicting relative rates and equilibrium constants.

In order to evaluate the field model, the data in Table I were analyzed by means of the Tanford modification of the Kirkwood–Westheimer cavity model.[13] The parameters used in the calculation as well as the calculated and experimental equilibrium constant ratios are listed in Table II. While agreement is only qualitatively good, the field model does predict the correct order of acidities.

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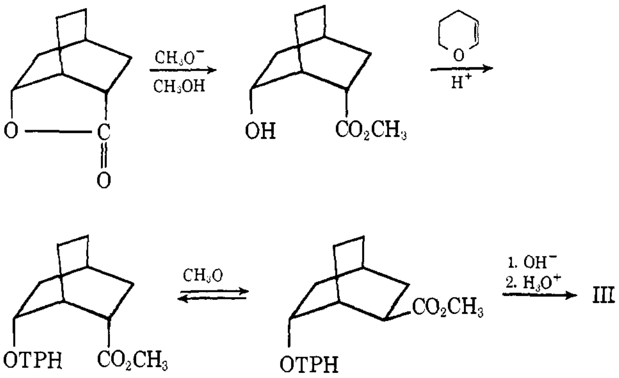
(6) Mixtures of the ethyl esters of I and II were prepared from ethyl *endo*-bicyclo[2.2.2]oct-2-ene-5-carboxylate (V) by two methods: (a) oxymercuration–demercuration[7] and (b) hydroboration followed by oxidative work-up.[8] The corresponding acetates were separated by silica gel column chromatography and subsequently hydrolyzed to I and II. III was prepared by the following scheme



IV was prepared by catalytic hydrogenation of V followed by hydrolysis. The melting points of I, II, III, and IV are 150–150.5, 111.5–112.5, 136.5–138, and 83–84.5° (lit.[9] 84–85°), respectively. All spectral data (nmr, ir, and mass spectral) and all neutralization equivalents were consistent with the assigned structures.

(7) H. C. Brown and F. Geogphegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(8) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

(9) R. Seka and O. Tramposh, *Ber. Deut. Chem. Ges. B*, **75**, 1379 (1942).

(10) The pK_a values were determined by a previously described method: C. L. Liotta, K. H. Leavell, and D. F. Smith, Jr., *J. Phys. Chem.*, **71**, 3091 (1967).

(11) According to the σ-inductive model,[12] if one considers a substituent at a position S on a molecule, the polarization of the bond between the substituent and the atom to which it is attached can be transmitted to another position on the molecule, $S + n$, n bonds removed from the point where the initial effect was exerted, by the successive polarization of the intervening σ bonds. The resultant effect, $\lambda_{S\pm n}$, will be equal to the initial effect, λ_S, multiplied by a constant factor per bond ($1/f < 1$) and summed over all pathways as illustrated by the following equation

$$\lambda_{S\pm n} = \lambda_S \sum_p [(1/f)^{(S\pm n)}]_p$$

(12) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).

(13) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); J. G. Kirkwood and F. H. Westheimer, *ibid.*, **6**, 513 (1938); F. H. Westheimer, W. A Jones, and R. A. Lad, *ibid.*, **10**, 478 (1942); F. H. Westheimer and M. W. Shookhoff, *J. Amer. Chem. Soc.*, **61**, 555 (1939); C. Tanford, *ibid.*, **79**, 5348 (1957).

(14) NSF Undergraduate Research Participant, Summer 1971.

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3-Vinylpentadienyl Anions. Rearrangement of 3-Vinylheptadienyl Anion to 2-Ethylcycloheptadienyl Anion

Sir:

According to HMO calculations, 3-vinylpentadienyl anions ($DE_\pi = 2.00\beta$) should have almost as much resonance stabilization as 1-vinylpentadienyl (=heptatrienyl) anions ($DE_\pi = 2.05\beta$). Although 3-vinylpentadienyl cations have been studied,[1] the only report involving one of the corresponding anions describes the use of the parent anion as an intermediate in the synthesis of tetravinylmethane,[2] and the spectral properties of the anion were not given. We wish to report the high-yield preparation and some nmr spectral properties of five cross-conjugated anions of this class, and the unexpectedly facile thermal rearrangement of one

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(1) T. S. Sorensen, *Can. J. Chem.*, **43**, 2744 (1965).

(2) J. G. Berger, E. L. Stogryn, and A. A. Zimmerman, *J. Org. Chem.*, **29**, 950 (1964).